

TN 295

. U4

8806

1979



IC

8806

B. u. l

Bureau of Mines Information Circular/1979

C-337
102



Citrate Process Demonstration Plant Design



UNITED STATES DEPARTMENT OF THE INTERIOR

3
Information Circular 8806

Citrate Process Demonstration Plant Design

By W. I. Nissen and R. S. Madenburg



UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

U. S. 2
BUREAU OF MINES
Lindsay D. Norman, Acting Director

The work upon which this report is based was done under an agreement between the Bureau of Mines, U.S. Department of the Interior, U.S. Environmental Protection Agency, and St. Joe Minerals Corp.

TN295
U4
8806, 1979

This publication has been cataloged as follows:

Nissen, William I

Citrate process demonstration plant design / by W. I. Nissen and R. S. Madenburg. [Washington] : U.S. Dept. of the Interior, Bureau of Mines, 1979.

16 p. : ill. ; 27 cm. (Information circular • Bureau of Mines ; 8806)

Bibliography: p. 15-16.

I. Flue gases • Desulphurization. I. Madenburg, R. S., joint author. II. United States. Bureau of Mines. III. Title. IV. Series: United States. Bureau of Mines. Information circular • Bureau of Mines ; 8806.

TN23.U71 no. 8806 622.06173

U.S. Dept. of the Int. Library

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
George F. Weaton powerplant host site.....	3
Citrate Process FGD demonstration plant.....	4
Ash removal and gas cooling.....	5
SO ₂ absorption.....	6
Solution regeneration and sulfur precipitation.....	7
Sulfur recovery.....	8
Sulfate removal.....	9
Hydrogen sulfide generation.....	9
Environmental impact.....	10
Operational testing and evaluation.....	11
Summary.....	14
References.....	15

ILLUSTRATIONS

1. George F. Weaton powerplant.....	4
2. Powerplant stack gas SO ₂ scrubbing--citrate process.....	5
3. Artist's concept of citrate process demonstration plant at the George F. Weaton powerplant.....	12
4. Citrate process demonstration plant model.....	13

CITRATE PROCESS DEMONSTRATION PLANT DESIGN

by

W. I. Nissen¹ and R. S. Madenburg²

ABSTRACT

This Bureau of Mines report presents the design for a commercial-sized flue gas desulfurization (FGD) demonstration plant that uses the citrate process. The goal of the Bureau's citrate process is to minimize the undesirable environmental impacts of industrial plants emitting SO_2 -bearing gas. The FGD plant is located at the George F. Weaton powerplant, Monaca, Pa. Construction was completed in April 1979 and will be followed by preliminary testing and a 1-year testing and evaluation program. Design capacity of the FGD plant is 156,000 scfm of 0.2-volume-percent- SO_2 flue gas yielding about 16 tons of sulfur per day. The plant is intended to (1) clean fly ash, SO_3 , and Cl^- from the gas while cooling the gas in a venturi scrubber, (2) absorb SO_2 from the gas using 1,200 gpm of a countercurrent-flowing citric acid-sodium citrate-sodium thiosulfate solution, (3) react the absorbed SO_2 in two 13,000-gal stirred closed vessels with added H_2S , thus precipitating elemental sulfur and regenerating the citrate solution for recycle, and (4) recover the sulfur from the slurry by air flotation, followed by melting in a heat exchanger and separation from the occluded citrate solution in a sulfur decanter at 35 psi and 135° C.

INTRODUCTION

In 1968 the Department of the Interior's Bureau of Mines started research on FGD with particular emphasis on control of SO_2 emissions from nonferrous smelters. This research was conducted in an effort to meet the Bureau's goal of minimizing the undesirable environmental impacts of mineral processing operations. Pioneering research had indicated that flue gas desulfurization might be achieved effectively by the absorption of sulfur dioxide (SO_2) in a suitable solution, followed by reaction of the absorbed SO_2 with gaseous hydrogen sulfide (H_2S) to precipitate sulfur and regenerate the solution for recycle. After a year of screening many possible reagent combinations of inorganic and organic solutions, it was established that an aqueous solution of citric acid

¹ Research supervisor, Salt Lake City Metallurgy Research Center, Bureau of Mines, Salt Lake City, Utah.

² Technical manager, citrate process demonstration plant, Morrison-Knudsen Co., Inc., Boise, Idaho.

and sodium citrate was an effective absorbent for SO_2 . Among the desirable characteristics affecting the choice of citrate were its good chemical stability, low vapor pressure, and adequate pH-buffering capacity, and the purity and physical character of the precipitated sulfur.

As first studied in the laboratory, the citrate process comprised (1) absorbing SO_2 in citrate solution, (2) reacting the absorbed SO_2 with H_2S , (3) filtering and melting the precipitated sulfur, and (4) recycling the regenerated citrate solution to the SO_2 absorption step. Preparation of the H_2S required for the precipitation step of the citrate process was studied separately. Hydrogen sulfide was generated by reacting recycle sulfur, natural gas, and steam over an alumina catalyst.

In 1970-71, a pilot plant to remove SO_2 flue gas from a copper reverberatory furnace was constructed and operated jointly by the Bureau of Mines and the Magma Copper Co. This plant, located at a smelter in San Manuel, Ariz., treated 300 scfm of gas containing 1.0 to 1.5 percent SO_2 and consistently removed 93 to 99 percent of the SO_2 . Results of the initial laboratory and pilot plant research were reported (3, 11).³

The preliminary Bureau of Mines laboratory and pilot plant research demonstrated that the citrate process is capable of substantially complete removal of SO_2 from industrial waste gases. Most of the SO_2 is converted to sulfur with less than 1.5 percent converted to sulfate regardless of the SO_2 and oxygen content of the feed gas. The citrate process produces an elemental sulfur end product that can be marketed or stored with a minimum of environmental disturbance.

After the encouraging preliminary results, two other pilot plant investigations were undertaken to obtain data for engineering evaluation and cost estimates. One pilot plant was independently built and operated by Arthur G. McKee and Co.,⁴ Peabody Engineered Systems, and Pfizer, Inc., at Terre Haute, Ind. (1-2, 4, 13). This operation treated a stack gas from a coal-fired steam-generating station that simulated a utility application. After several modifications to arrive at a final equipment configuration, the plant operated from March 15 to September 1, 1974, logging 2,300 operating hours. The longest sustained run was 180 hours. The plant consistently removed 95 to 97 percent of the SO_2 from flue gas containing 0.1 to 0.2 percent SO_2 .

The other pilot plant was constructed by the Federal Bureau of Mines and operated jointly by the Bureau and the Bunker Hill Co. at the latter's lead smelter in Kellogg, Idaho (6-10, 12). Nominal capacity of the plant was 1,000 scfm of 0.5-percent SO_2 gas, yielding about 600 pounds of sulfur per day. This pilot plant was operated between January 1974 and May 1976 for 5,400 hours and produced 55 net short tons of sulfur. The operation demonstrated that (1) more than 95 percent of the SO_2 could be removed from the lead smelter

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

⁴Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

sintering furnace tail gases, (2) regeneration of the citrate solution with H_2S and precipitation of sulfur in conventional stirred vessels was readily controlled and highly efficient, (3) the precipitated sulfur could be continuously recovered as a 99.5-percent-pure product by kerosene flotation and melting, and (4) the 77- to 79-percent- H_2S gas used for sulfur precipitation could be readily produced from pilot plant product sulfur, natural gas, and steam.

During 1975, plans were made for the construction and operation of a large-scale plant to demonstrate the applicability of the citrate process for FGD at powerplants burning high-sulfur coal. On June 1, 1976, the Bureau awarded a contract to the St. Joe Minerals Corp. for commercial-scale demonstration of the citrate process. The host site for the plant is St. Joe's George F. Weaton powerplant near Monaca, Pa. (5). This demonstration plant is being constructed and will be operated under a cooperative arrangement on a cost-sharing basis between the Bureau, the U.S. Environmental Protection Agency, and St. Joe. The design, construction, and maintenance of this plant were contracted to the Morrison-Knudsen Co., with the Ralph M. Parsons Co. providing engineering services. Radian Corp., under contract to the Bureau, will independently test and evaluate the operation.

The present report describes the George F. Weaton powerplant host site, the citrate process FGD plant design, the environmental impact, and operational testing and evaluation.

GEORGE F. WEATON POWERPLANT HOST SITE

The citrate process FGD demonstration plant is being retrofitted to St. Joe's George F. Weaton powerplant located on the south bank of the Ohio River at Monaca, Pa., near Pittsburgh (fig. 1). This powerplant is a base-loaded, coal-fired electricity-generating plant operating at a unit load factor of approximately 90 percent on a 24-hour-per-day and 7-day-per-week basis. The powerplant consists of two identical units, each capable of supplying 60 Mw of electrical energy to St. Joe's nearby zinc smelter. In addition, the powerplant can interchange 25 Mw of electrical power with the Duquesne Light Co. The host powerplant has a conventional tangentially fired, pulverized-coal-burning boiler and utilizes a direct-coupled boiler-turbine generator arrangement. The main steam flow is 450,000 lb/hr at 1,000° F and 1,850 psig with integral reheat steam of 334,000 lb/hr at 1,000° F and 424 psig for each boiler at maximum load. The overall powerplant heat rate is approximately 10,000 Btu/kwhr. Boilers operate with five stages of feed water heating and utilize steam-turbine-drive boiler feed pumps. Each boiler has its own economizer, superheater, combustion air preheaters, draft fans, and combustion control for independent operation.

Approximately 85,000 tons of coal is stockpiled adjacent to the powerplant. This coal is transported by belt conveyor to coal hoppers at the powerplant. Coal from these hoppers is pulverized and fired in the powerplant boilers. For the purpose of the citrate process demonstration, coal will contain from 2.5 to 4.5 percent sulfur and less than 15 percent ash.

Particulate control is achieved through a combination mechanical and two-stage electrostatic precipitator which removes over 99.6 percent of the fly ash.

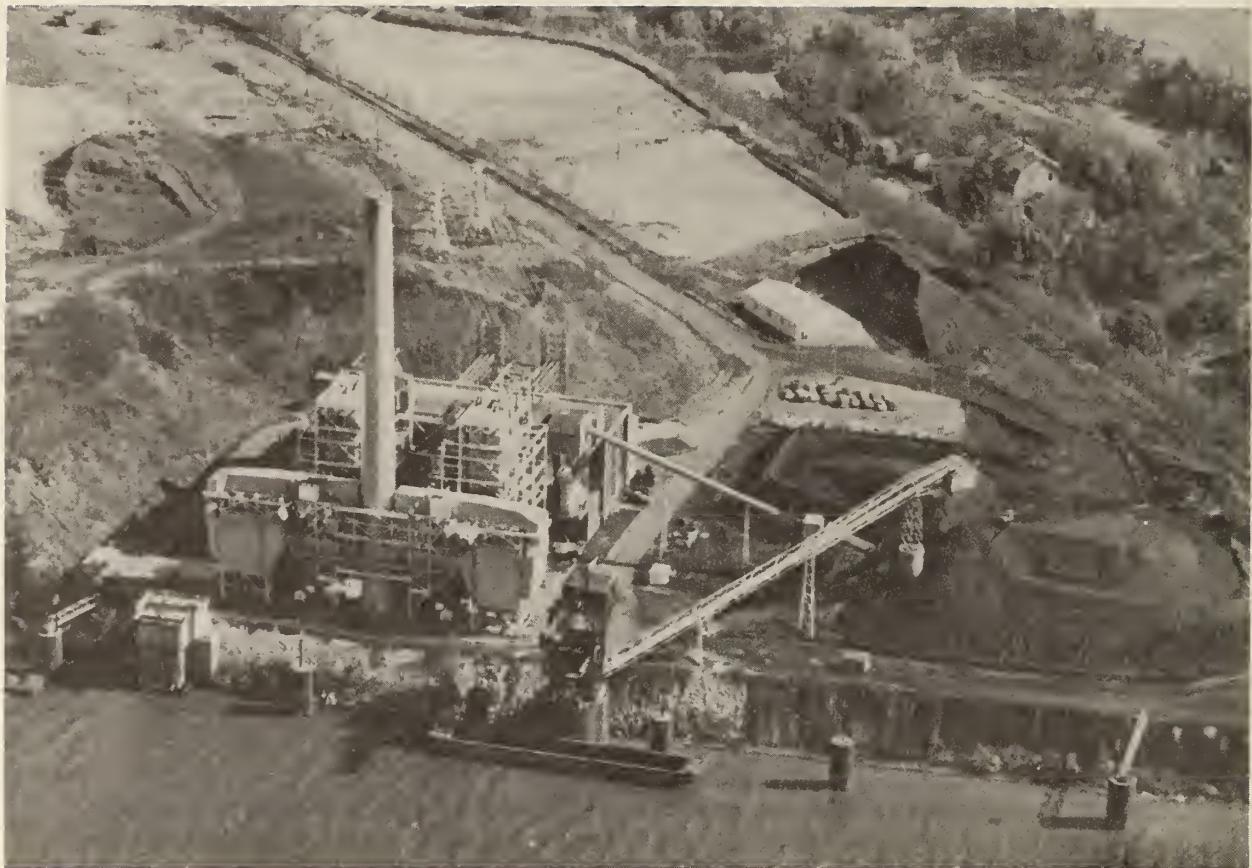


FIGURE 1. - George F. Weston powerplant.

Bottom ash from the boilers and fly ash from the precipitators are conveyed to a settling pond for decantation, drying, and subsequent disposal.

CITRATE PROCESS FGD DEMONSTRATION PLANT

Construction of the citrate process FGD demonstration plant was completed at the end of April 1979. As shown in the generalized process flowsheet (fig. 2), the citrate process will draw SO_2 -bearing flue gas from the duct between the existing electrostatic precipitator and the stack. The nominal design capacity of this plant is 156,000 scfm of 0.2-percent- SO_2 gas, which at 90 percent SO_2 removal and 2 percent SO_2 oxidation will yield approximately 16 tons of sulfur per day. The plant will have six specific unit operations, as follows:

1. Residual fly ash removal and gas cooling.
2. SO_2 absorption.
3. Solution regeneration and sulfur precipitation.
4. Sulfur recovery.
5. Sulfate removal.
6. H_2S generation.

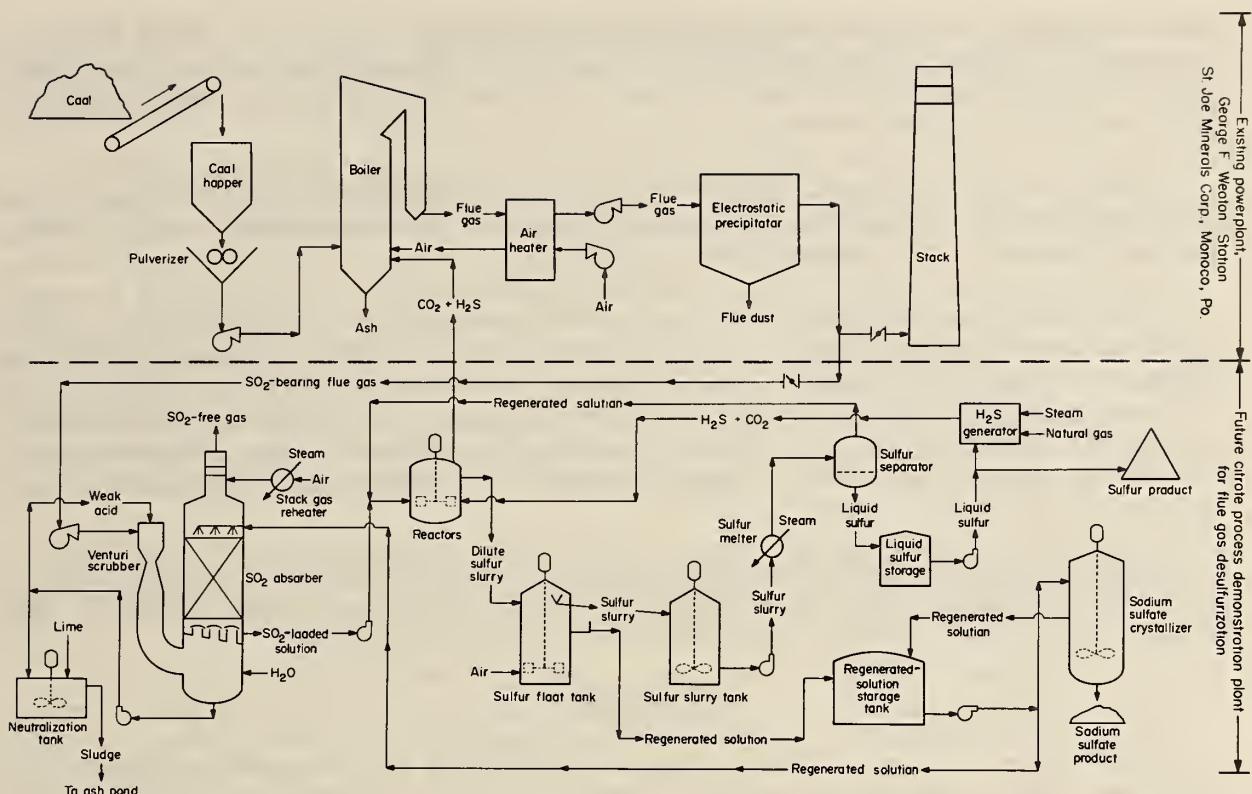


FIGURE 2. - Powerplant stack gas SO₂ scrubbing-citrate process.

The design parameters, design features, and process equipment for these six unit operations follow.

Ash Removal and Gas Cooling

A forced-draft fan transports the flue gas through a 10-foot-diameter duct to the plant. This fan is a double-inlet mechanical-draft type which will deliver in normal operation 234,000 actual cubic feet per minute at 300° F and a discharge pressure of 9.7 inches of water. The fan is constructed of carbon steel and is driven by a 1,000-hp electric motor.

Downstream of the fan, an eductor-type venturi scrubber removes residual fly ash, sulfur trioxide (SO_3), and chlorides (Cl^-) from the flue gas. This venturi also cools the gas from 300° to 120° F by both humidification and sensible cooling. Sensible cooling requires high solution recirculation rates, and the eductor design utilizes a 4,500-gpm flow at 40 psig at the nozzle to reduce the fan requirement. Venturi scrubber solution and flue gas separate in the bottom of the vessel that contains the SO_2 absorber. Except for a bleed stream, most of the solution recycles to the venturi scrubber. Two pumps in series transport the recycle solution through a heat exchanger. These pumps are the centrifugal, horizontal slurry type and will deliver 4,500 gpm in normal operation. The pump casings and impellers are rubber-lined cast iron with Hastelloy C trim. Each pump is driven by a 250-hp electric motor. The

heat exchanger cools the recycle solution from 120° to 112° F. This heat exchanger is designed to exchange 19.8×10^6 Btu/hr and is a plate type fabricated of palladium-stabilized titanium. Makeup water replaces the humidification and bleed stream losses.

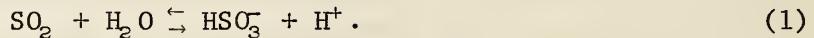
The venturi scrubber, which is 10 feet in diameter by 45 feet high, has an acid-proof brick and rubber membrane lining over a carbon steel shell. The venturi nozzle is fabricated from Inconel 625.

The bleed stream removes ash and acids and prevents their buildup. This bleed stream flows through a 2-foot-diameter by 18-foot-high scrubber effluent stripper packed with about 31 cubic feet of 1-inch polypropylene saddles. At the same time that the bleed stream flows through the stripper, a 100-scfm stream of air flows countercurrently, strips any absorbed SO_2 , and returns the SO_2 to the absorption tower. The stripper is fabricated of fiberglass-reinforced polyester (FRP).

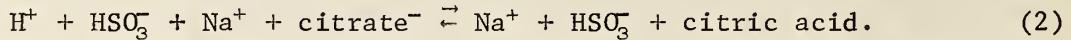
The SO_2 -stripped bleed stream flows to an acid-brick-lined, agitated, concrete tank where lime is added to neutralize acids. A pump transfers the neutralized bleed stream to the existing ash-settling pond.

SO_2 Absorption

The cooled, cleaned flue gas passes through a chlorinated polyvinyl chloride (CPVC) chevron entrainment separator and a chimney tray having four 6-1/2-foot-diameter chimneys into the SO_2 absorber. The flue gas flows upward through a 26-foot-diameter by 20-foot-high packed bed of 2-inch polypropylene saddles countercurrent to citrate solution. This citrate solution is a 0.5-molar citric acid solution buffered with sodium base to a pH between 4.5 to 4.7 and contains about 0.25 molar sodium thiosulfate. In the SO_2 absorber more than 90 percent of the SO_2 is removed from the flue gas by the following reaction:



Reaction 1 is enhanced by the buffering properties of the citrate solution illustrated in reaction 2:



The hydrogen ion produced by absorption of SO_2 in reaction 1 combines with a citrate ion in reaction 2 to form citric acid, an un-ionized acid. The treated flue gas then passes through a CPVC chevron entrainment separator into a 10-foot-diameter by 105-foot stack mounted on top of the absorber vessel, which is 95 feet high. When required by ambient conditions, steam-heated air reheats the treated flue gas to aid dispersion.

The SO_2 absorber and stack are fabricated of carbon steel. The absorber is lined with vinylester reinforced with glass flakes. A Penngard lining is used in the reheat zone between the absorber and the stack. The Penngard

lining consists of a corrosion-resistant asphaltic membrane covered with a lightweight heat- and corrosion-resistant insulating brick. The stack is protected with an FRP sleeve.

A pump transports the SO_2 -rich citrate solution from the SO_2 absorber to the solution regeneration and sulfur precipitation section. This pump is a centrifugal, horizontal, single-stage type which will deliver 1,200 gpm in normal operation. The pump is constructed of Chlorimet 3 with Hastelloy C trim and is driven by a 40-hp electric motor. After regeneration, another pump recycles the SO_2 -lean citrate solution from a citrate storage tank back to the SO_2 absorber. This lean-solution pump is similar to the rich-solution pump except that it is driven by a 120-hp motor. During lean-solution recycle, a heat exchanger cools the solution from 131° to 123° F with river water. This heat exchanger is designed to exchange 5.4×10^6 Btu/hr and is a plate type fabricated of palladium-stabilized titanium.

Also in the SO_2 absorber, the water balance of the process is controlled by vaporization. Water additions come primarily from the solution regeneration reaction, the caustic makeup, and the gas from the H_2S generator.

To vaporize water in the absorber, saturated flue gas entering at 120° F contacts lean citrate solution entering at 123° F. The exiting flue gas, which is heated by the 3° F temperature differential, remains saturated by vaporization of water from the citrate solution.

Solution Regeneration and Sulfur Precipitation

Rich citrate solution leaving the absorber flows in series through two tandem 13,000-gallon-capacity reactors. These reactors are 12-foot-diameter by 18-foot-high carbon steel vessels, which are lined with vinyl ester reinforced with glass flakes. In the reactors, SO_2 -rich solution reacts with an $\text{H}_2\text{S}-\text{CO}_2$ gas from the H_2S generator according to the following overall reaction to regenerate the solution and precipitate sulfur:



The $\text{H}_2\text{S}-\text{CO}_2$ gas flows into the second of the two reactors through a sparger underneath an agitator which disperses the gas into the solution. The H_2S gas that does not react in the second reactor flows into the first reactor through a sparger. Again, an agitator disperses the gas. The agitators each have a 67-inch-diameter, four-blade radial impeller which turns at 68 rpm approximately 4 feet from the bottom of the reactor. The agitators are turned by 100-hp electric motors. All wetted parts of the agitators are Inconel 625.

Offgas, which is mainly CO_2 with small quantities of H_2S , CS_2 , and COS from the reactor system, flows to the boiler firebox for incineration to SO_2 . Slurry flows by gravity through the reactor system, which is stepped, to a digester. The digester is physically similar to the reactors except the agitator has an axial impeller driven by a 3-hp motor. In the digester, any dissolved or entrained H_2S in the slurry reacts with a small stream of SO_2 -rich solution from the absorber. From the digester, the slurry flows by gravity to the sulfur flotation tank.

Sulfur Recovery

Sulfur separates from the bulk of the solution by air flotation in an agitated 18,500-gallon-capacity tank. The flotation tank is 15 feet in diameter by 20 feet high and is made of carbon steel, which is lined with vinyl ester reinforced with glass flakes. In the tank, sulfur froth, aided by air, floats on the surface of the solution. A lobe-type blower supplies air to the tank, and a 25-hp turbo agitator, which has Hastelloy C-276 wetted parts, disperses the air throughout the solution. The sulfur froth, which is concentrated to about 10 percent solids, flows over a weir to an agitated 18,000-gallon-capacity sulfur slurry tank.

The sulfur slurry tank is 15 feet in diameter by 20 feet high and is made of carbon steel, which is lined with vinyl ester reinforced with glass flakes. The sulfur slurry tank agitator degasses the sulfur froth and suspends sulfur crystals in the solution. The agitator, which turns at 45 rpm, has two 42-inch-diameter, four-blade radial impellers. All wetted parts of the agitator are Inconel 625.

Regenerated lean citrate solution flows from the bottom of the flotation tank through an adjustable overflow weir box that allows adjustment in the solution level in the flotation tank. The weir box is fabricated of FRP with Hastelloy C trim. Lean citrate solution from the weir box flows by gravity to a 125,000-gallon-capacity citrate storage tank, which is made of carbon steel, which is lined with vinyl ester reinforced with glass flakes.

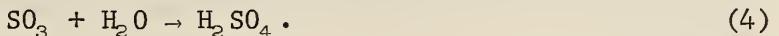
Vapor spaces of all tanks downstream of the reactor system are piped into an exhaust system. An exhaust fan draws vapors containing traces of H_2S and COS and discharges these vapors into the boiler firebox for incineration to SO_2 . SO_2 generated from the combustion of H_2S and COS is recycled to the citrate process plant for desulfurization.

Sulfur is separated from the remaining solution by heating the sulfur slurry from 131° F to about 260° F and melting the sulfur with steam in a concentric tube heat exchanger. A progressing cavity-type pump transports 64 gpm of sulfur froth from the sulfur slurry tank to the heat exchanger. This pump has Hastelloy C and rubber wetted parts and is driven by a 20-hp electric motor. The heat exchanger is designed to exchange 4.11×10^6 Btu/hr, operates at a pressure of about 35 psig, and is a jacketed-pipe type with the tube and shell fabricated of Hastelloy C-276 and carbon steel, respectively. The liquid sulfur separates from the citrate solution by gravity in a 850-gallon sulfur separator. The sulfur separator is a pressurized, steam-jacketed decanter vessel fabricated of Hastelloy C-276-clad carbon steel. Liquid sulfur, which has a purity of greater than 99.5 percent, flows from the bottom of the sulfur separator to a 56,000-gallon, heated, carbon steel storage tank. The citrate solution flows from the top of the sulfur separator to the first reactor in the solution regeneration and sulfur precipitation operation.

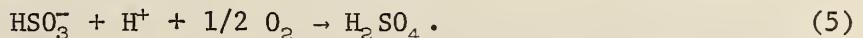
A filter removes solid impurities from the liquid sulfur, and a pump transfers one-third of the liquid sulfur to load out for marketing or storage. Another pump transfers the other two-thirds of the liquid sulfur to the H_2S generator, where it is used to manufacture H_2S gas. The sulfur load-out pump, which will pump 50 gpm at 260° F and a 20-psi differential pressure, is driven by a 3-hp electric motor and has a cast steel case and cast iron impeller. The sulfur transfer pump will pump 15 gpm at 260° F and a 72-psi differential pressure, is driven by a 3-hp electric motor, and has a cast iron case and impeller.

Sulfate Removal

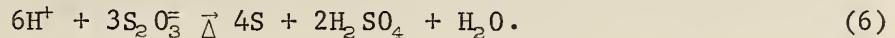
Up to 1.5 percent of the sulfur contained in the flue gas forms sulfuric acid (H_2SO_4) rather than sulfur in the citrate process. Sulfur trioxide, SO_3 , contained in the flue gas may be absorbed in the citrate solution by the following reaction:



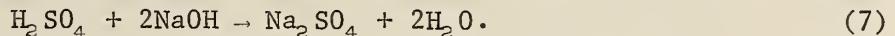
Absorbed sulfur dioxide, SO_2 , in the form of HSO_3^- ion may be oxidized during absorption by the following reaction:



Thiosulfate ion, $S_2O_3^{2-}$, which is a sulfur compound formed during solution regeneration, decomposes during sulfur melting by the following reaction:



Caustic (NaOH) neutralizes the H_2SO_4 and forms sodium sulfate (Na_2SO_4) in solution by the following reaction:

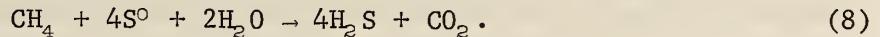


Glauber salt ($Na_2SO_4 \cdot 10H_2O$) crystallizes from a chilled citrate solution, which provides a method to remove the buildup of Na_2SO_4 from the solution.

A vacuum-cooled crystallizer cools a bleed stream of citrate solution and crystallizes glauber salt. The capacity of the crystallizer is approximately 4 tons of glauber salt per day. Wetted parts of the crystallizer are FRP, Hastelloy, or rubber-lined carbon steel.

Hydrogen Sulfide Generation

Recovered elemental sulfur (S^0), natural gas (CH_4), and steam (H_2O) as consumptive feed stocks react to form H_2S according to the following reaction:



An onsite H_2S generator produces about 35 tons of H_2S per day in a fixed-bed catalytic reactor. The design of the H_2S generator is based on a proprietary process developed by Home Oil Co. Ltd. of Calgary, Alberta, Canada, as modified and pilot-plant-tested by the Bureau of Mines.

The H_2S generator is designed so that reaction 8 is at least 95 percent efficient. Impurities besides CO_2 and H_2O include CS_2 and COS . Materials of construction for the H_2S generator process include suitable stainless steels, Alonized stainless steel, and stainless steel lined with high-temperature refractories. Additionally, the H_2S generator is designed and constructed to operate using a carbon monoxide reductant should natural gas supplies become unavailable.

ENVIRONMENTAL IMPACT

The citrate process produces high-purity elemental sulfur and industrial-grade glauber salt. The National Environmental Policy Act of 1969 requires the identification and disposition of all the product and waste streams associated with the citrate process demonstration plant. The following list identifies those known and anticipated product or waste streams and states their disposition:

Treated flue gas, 156,000 scfm.--Flue gas will discharge to the atmosphere and will contain approximately 0.02 volume-percent SO_2 .

Product sulfur, 16 tons per day.--High-purity elemental sulfur will be used as a feed stock in St. Joe's sulfuric acid plants.

Byproduct glauber salt, 5 tons per day (80 percent solids).--Industrial-grade glauber salt will be marketed or disposed of in an environmentally acceptable manner (chemical landfill).

Venturi scrubber bleed stream, 72 tons per day (5.5 percent solids).-- The bleed stream will contain about 1-1/2 tons of fly ash per day and will be neutralized with lime. The neutralized sludge, which will contain about 1 ton of CaCl_2 and 1-1/2 tons of CaSO_4 per day, will join the powerplant's fly ash disposal stream, which contains about 120 tons of fly ash per day. Fly ash and other solids settle in ponds.

Cooling and condensate water streams.--Water streams that are not recycled will be discharged in an environmentally acceptable manner.

H_2S gas during startup and transient conditions.-- H_2S gas not utilized by the process will be incinerated to SO_2 . The maximum SO_2 emission to the atmosphere during startup will be 3,300 pounds of SO_2 per hour for 30 minutes for a total emission of 1,650 pounds of SO_2 . The maximum SO_2 emission to the atmosphere during upset conditions⁵ will be 6,600 pounds of SO_2 per hour for 10 minutes, or a total emission of 1,100 pounds of SO_2 . During the demonstration year of operation, two startup periods are expected. Upset conditions are estimated to take place no more than once a week and are expected to be of short duration. The emissions resulting from startup or transient conditions will be eliminated or minimized as experience is gained in operating and effectively using the installed instrumentation for process operation and control.

Combustion gases from the sulfur superheater.--These gases result from firing No. 2 fuel oil containing 0.3 percent sulfur and will be discharged to the atmosphere after waste heat recovery.

⁵Upset conditions may include failure of the process chemistry, failure of the plant equipment, or interruption of process flows.

Vent gas from the sulfur precipitation reactors.--This gas, containing mostly CO₂ with traces of H₂S, COS, CS₂, and CH₄, will flow to the powerplant boiler for incineration to SO₂ for recycle to the citrate process demonstration plant.

Vent gases from the flotation tank, sulfur slurry tank, and citrate storage tank.--These vent gases may contain traces of COS, CS₂, and H₂S and will flow to the powerplant boiler for incineration to SO₂ for recycle to the citrate process demonstration plant.

Sulfur filter cake, 300 pounds per week.--This filter cake, containing mainly sulfur and diatomaceous earth with minor amounts of citrate salts and fly ash, will be disposed of in an environmentally acceptable manner.

Citrate solution, leaks or spills.--Leaks and spills of citrate solution will be collected in a common sump and recycled to the process.

OPERATIONAL TESTING AND EVALUATION

The citrate process demonstration plant will be tested and evaluated for 1 year following acceptance. The objectives of these tests are--

1. To characterize the citrate system with respect to the operating parameters.
2. To determine the citrate system's optimum operating conditions.
3. To determine long-term system reliability.
4. To determine the environmental impact of the citrate system.
5. To determine the technical and economic feasibility of the citrate system.
6. To document the results of the test program.

The Bureau has retained the Radian Corp. to serve as an independent, unbiased test and evaluation contractor. Radian will develop and implement a test plan that includes--

1. Baseline testing, which will be divided into two distinct segments. One segment will observe actual boiler operation over about 4 weeks, while monitoring all available boiler operating parameters and effluent discharges. The second segment of the baseline testing will investigate the historical limits of boiler operation. This segment will be executed during the same testing period. The coordination of these two segments will insure that the boiler is operating at historically normal conditions during the test period.

2. Acceptance testing, which will be performed to certify that the citrate process demonstration plant will meet performance guarantees. The acceptance test will require the system to operate for a period of not less

than 10 consecutive days while burning coal containing not less than 2.5 percent sulfur and meeting both the New Source Performance Standards and a 90-percent- SO_2 -removal standard.

3. Optimization of the system, which will be investigated through the 1-year demonstration period. Data collected during the demonstration testing will be used to determine what adjustments are required to optimize plant operations (a) to minimize absorber liquid-gas ratio, system pressure drop, reagent and feed stock consumption, power and utility consumption, and process costs and (b) to maximize SO_x removal, particle removal, system reliability, and system availability.

4. Documentation of the citrate system's performance, which will include reliability, availability, and utilization information. For proper overall power station operation, FGD system availability should be maintained at high

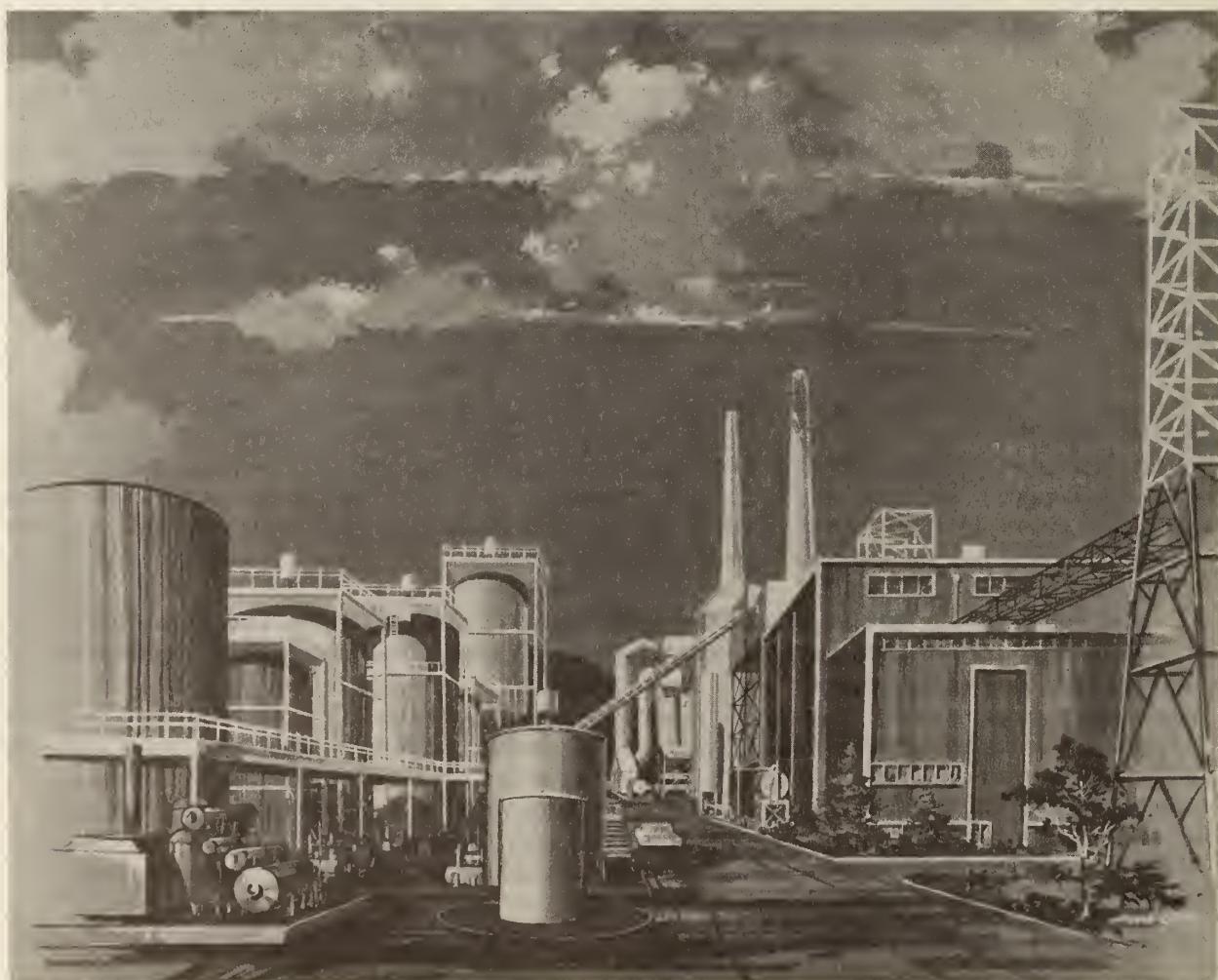


FIGURE 3. - Artist's concept of citrate process demonstration plant at the George F. Weston powerplant.

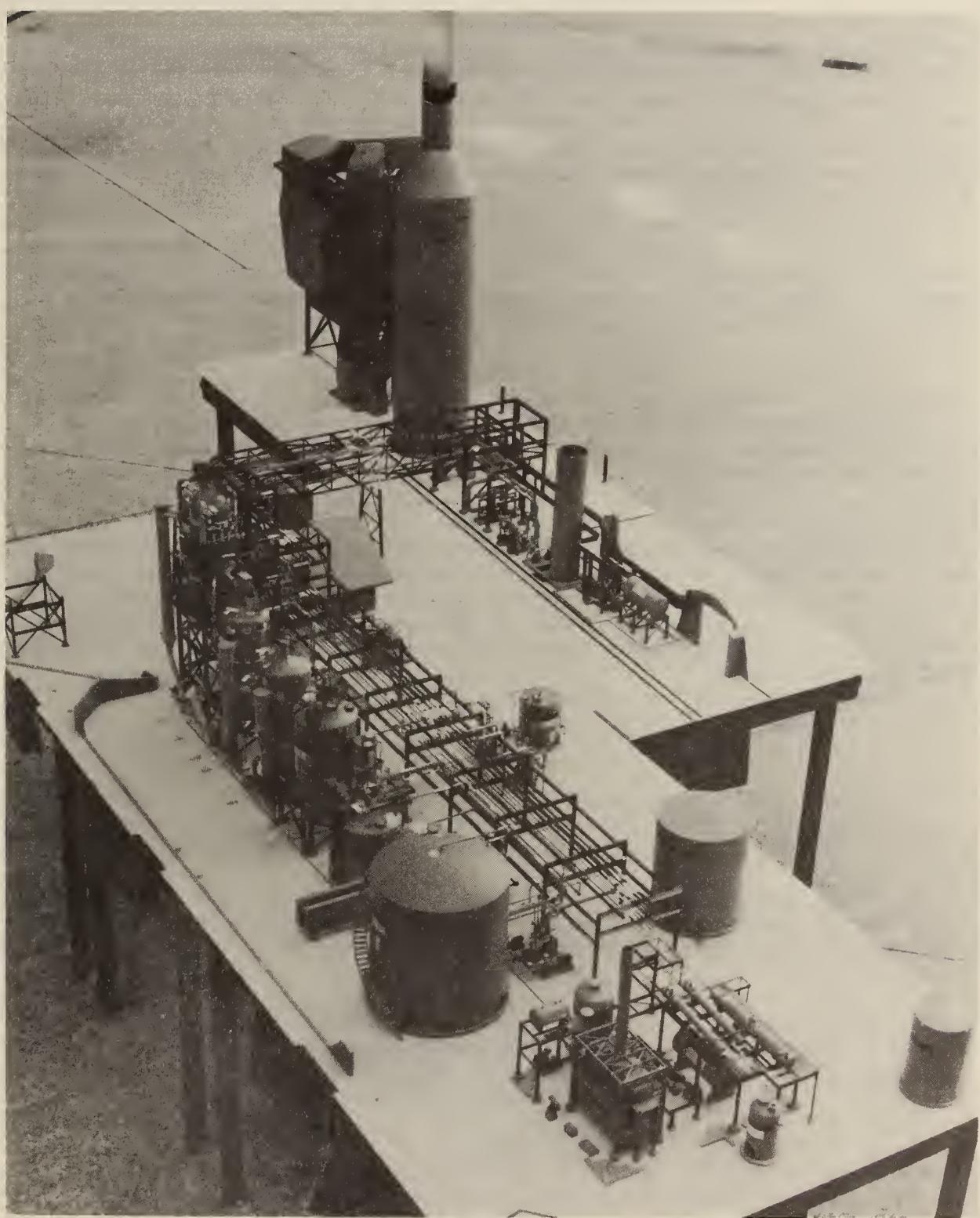


FIGURE 4. - Citrate process demonstration plant model.

levels. Information concerning boiler and citrate system operation will be gathered daily and reported monthly. System performance will be reported in terms of availability, reliability, and utilization. Availability is defined as the percentage of a given time period that the FGD system is available for operation. Reliability is the percentage of instances that the FGD system operated when it was called upon to operate. Utilization is the percentage of time that the boiler operated during a time period and reflects the load demand imposed on the FGD system.

Special studies to investigate sulfate formation, system corrosion, materials evaluation, stack gas reheat, and other items of interest will also be conducted during this 1-year period. In addition, process economics will be developed based upon the demonstration project information.

SUMMARY

Figure 3 is an artist's concept of the citrate process demonstration plant at the George F. Weaton powerplant. The FGD plant is being constructed and will be operated on the 60-Mw Unit No. 1. Figure 4 is a photograph of the engineering design scale model, which assists in the construction of the plant. Design capacity of the FGD plant is 156,000 scfm of 0.2-percent SO₂ flue gas recovering over 90 percent of the SO₂ and yielding about 16 tons of sulfur per day. Studies conducted at this project will provide information for economic and technical comparison of the citrate process and other FGD systems. This information will be gathered during commercial-scale operation and will be useful for applying experience gained at the George F. Weaton facility to other systems.

REFERENCES

1. Chalmers, F. S. Citrate Process Ideal for Claus Tailgas Cleanup. *Hydrocarbon Processing*, v. 53, No. 4, April 1974, pp. 75-77.
2. Chalmers, F. S., L. Korosy, and A. Saleem. The Citrate Process To Convert SO_2 to Elemental Sulfur. Pres. at Industrial Fuel Conf., Purdue Univ., West Lafayette, Ind., Oct. 3, 1973, 7 pp.; available for consultation at the Salt Lake City Metallurgy Research Center, Bureau of Mines, Salt Lake City, Utah.
3. George, D. R., L. Crocker, and J. B. Rosenbaum. The Recovery of Elemental Sulfur From Base Metal Smelters. *Min. Eng.*, v. 22, No. 1, January 1970, pp. 75-77.
4. Korosy, L., H. L. Gewanter, F. S. Chalmers, and S. Vasan. Sulfur Dioxide Absorption and Conversion to Sulfur by the Citrate Process. Ch. 16 in *Sulfur Removal and Recovery From Industrial Processes*, ed. by John B. Pfeiffer (Advances in Chemistry Series 139). American Chemical Society, Washington, D.C., 1975, pp. 192-211.
5. Madenburg, R. S., and R. A. Kurey. Citrate Process Demonstration Plant, A Progress Report. EPA-600/7-78-0586, Proc., v. 2, March 1978, pp. 707-735.
6. McKinney, W. A., W. I. Nissen, L. Crocker, and D. A. Martin. Status of the Citrate Process for SO_2 Emission Control. Pub. in *Technology and Use of Lignite*, Proceedings of a symposium held at Grand Forks, N. Dak., May 14-15, 1975, compiled by W. R. Kube and G. H. Gronhovd. GFERC/IC-75/2, 1975, pp. 148-172.
7. McKinney, W. A., W. I. Nissen, D. A. Elkins, and J. B. Rosenbaum. Pilot Plant Testing of the Citrate Process for SO_2 Emission Control. EPA 650/2-74-126b, Proc., v. 2, December 1974, pp. 1049-1067.
8. McKinney, W. A., W. I. Nissen, and J. B. Rosenbaum. Design and Testing of a Pilot Plant for SO_2 Removal From Smelter Gas. Pres. at Ann. Meeting, AIME, Dallas, Tex., Feb. 23-28, 1974, AIME Preprint A-74-85, 12 pp.
9. Nissen, W. I., L. Crocker, and D. A. Martin. Lead Smelter Flue Gas Desulfurization by the Citrate Process. Ch. 52 in *World Mining and Metals Technology*, ed. by Alfred Weiss (Proc. Joint MMJ-AIME Meeting, Denver, Colo., Sept. 1-3, 1976), Port City Press, Baltimore, Md., v. 2, 1976, pp. 825-854.
10. Nissen, W. I., D. A. Elkins, and W. A. McKinney. Citrate Process for Flue Gas Desulfurization, A Status Report. EPA-600/2-76-136b, Proc., v. 2, May 1976, pp. 843-864.

11. Rosenbaum, J. B., D. R. George, and L. Crocker. The Citrate Process for Removing SO₂ and Recovering Sulfur From Waste Gases. Pres. at AIME Environmental Quality Conf., Washington, D.C., June 7-9, 1971, 26 pp.; available upon request from the Salt Lake City Metallurgy Research Center, Bureau of Mines, Salt Lake City, Utah.
12. Rosenbaum, J. B., W. A. McKinney, H. R. Beard, L. Crocker, and W. I. Nissen. Sulfur Dioxide Emission Control by Hydrogen Sulfide Reaction in Aqueous Solution -- The Citrate System. BuMines RI 7774, 1973, 31 pp.
13. Vasan, S. The Citrex Process for SO₂ Removal. Chem. Eng. Prog., v. 71, No. 5, May 1975, pp. 61-65.

H 3 80 4





LIBRARY OF CONGRESS



0 002 959 997 A